Air Force Invention No. AFB00563

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#14 3/11/03 TC

On 19 February 2003
(DATE OF DEPOSIT)

Thomas C. Stover 22,531
NAME OF APPLICANT, ASSIGNEE, OR REG. REP.

T C Stover
SIGNATURE

19 February 2003
DATE

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re CIP Application of
Joseph D. Lichtenhan et al
Application Serial No. 09/783,719
Filed: 16 February 2001
For: **ALTERING OF POSS RINGS**

Group Art Unit: 1722
Examiner: M. Moore

Honorable Commissioner for Patents
Washington D. C. 20231

Sir:

**DECLARATION UNDER 37 CFR 1.132**

I, Joseph D. Lichtenhan of San Juan Capistrano, California, declare and say that:

1 I am one of the inventors in the above-identified application filed on 16 February 2001.

2. The recent Office Action dated 11-22-2002, states a belief that if one makes the endo compound, e.g., of Lichtenhan '867, one obtains such compound with the OH groups in the endo and exo positions and that a teaching of the endo compound, e.g., in '867, suggests the exo compound of present claim 18.

3. However, in our work in '867, we were only able to prepare endo OH groups and not exo OH groups by the disclosed method of the patent.

4. The stereo specific nature of silsesquioxanes has also been noted in the literature, see "Facile and Remarkably Selective Substitution..." by Frank Feher et. al *J. Am. Chem. Soc.*, 1997 vol 119, pp 3397-3398, attached hereto as Exhibit A.

5. Not until the inventive method of present claim 18 were we able to produce the exo OH isomer.

6. As to the assertion by the Office Action that the two isomers have similar properties, this has been determined not to be the case. That is, it has been found that the exo isomer has much higher reactivity because the SiOH has less steric hindrance than the SiOH of the endo isomer.

7 As to claims 20, 21 & 25; Declarant maintains that the method of Lichtenhan '562 could not produce an expanded ring having an RR substituent because that method uses a different reagent. That is, '562 teaches the use of a single R reagent, $Y_3SiR$.

8. However, claim 20 of the present application uses another reagent, i.e., $Y_2SiRR$ and arrives at novel RR products such as recited in claim 25, which could not be produced by the '562 method, inherently or otherwise.

9. I further declare that the statements made herein of my own knowledge are true and that all statements, made on information and belief, are believed to be true and furthermore that these statements are made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment or both under section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the above application or any patent issuing thereon.

February 18, 2003
Date

Joseph D. Lichtenhan, Declarant

*J. Am. Chem. Soc.* 1997, *119*, 3397−3398 

# Facile and Remarkably Selective Substitution Reactions Involving Fram work Silicon Atoms in Silsesquioxane Frameworks

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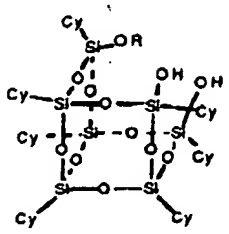
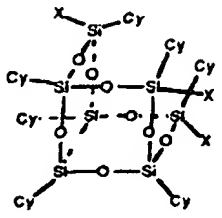
*Received November 12, 1996*

Over the past several years, incompletely-condensed silsesquioxane frameworks[1−5] (e.g., **1**−**2**) have attracted attention as models for silica,[6−9] as ligands in homogeneous models for aluminosilicates[10−14] and silica-supported catalysts,[15−20] as comonomers for new families of silsesquioxane-based polymers,[21,22] and as building blocks for network solids.[23] For all of these applications, any chemical modification of the silsesquioxane has involved reactions which transform SiOH groups into new siloxane (i.e., Si−O−Si) or heterosiloxane (i.e., Si−O−M) linkages. In this paper we report several facile and remarkably selective substitution reactions involving the framework silicon atoms of **1**. In addition to providing access to several versatile new starting materials, these reactions provide a powerful new methodology for functionalizing the rapidly expanding pool of incompletely-condensed silsesquioxane frameworks.

The reaction of **1** with excess $HBF_4$·$OMe_2$ occurs quickly upon mixing in $CH_2Cl_2/Et_2O$ or $CDCl_3$.[24] Rather than effecting cyclodehydration[2,6] or producing a stable salt derived from protonation of **1**, this reaction affords a quantitative NMR yield of a new $C_s$-symmetric Si/O framework, which was identified as **3** on the basis of multinuclear ($^1H$, $^{13}C$, $^{29}Si$, $^{19}F$) NMR data, mass spectral data, and a single-crystal X-ray diffraction study.[25] When performed on preparative scales in $CH_2Cl_2/Et_2O$, the reaction of **1** with excess $HBF_4$·$OMe_2$ spontaneously produces large, well-formed crystals of **3** in 96% after several days at 25 °C. However, it is clear from experiments performed in $CDCl_3$ in NMR tubes that the reaction is complete within 20 min and that only a slight excess (>5 equiv) of $HBF_4$ is required.



**1** R = H
**2** $SiMe_3$



**3** X = F
**4** $OSnMe_3$
**5** OH
**6** Me

The formation of a fluorine-containing framework was clearly signaled by the appearance of $^{19}F$-coupled resonances at $\delta$ 22.27 (d, $J$ = 24 Hz, 3 *C*H) in the $^{13}C$ NMR spectrum and $\delta$ −65.43 (d, $J$ = 24 Hz, 3 Si) in the $^{29}Si$ NMR spectrum as well as a prominent $^{19}F$ resonance at $\delta$ −138.0. The ORTEP plot from a preliminary X-ray crystal structure of **3** is shown in Figure 1. The molecule crystallizes in the space group *Pbca* with the three cyclohexyl groups adjacent to Si−F adopting mutually parallel orientations with respect to their Si−C vectors. This arrangement forces the silsesquioxane framework to adopt a substantially more open structure compared to **1**, but this structure can be accommodated within the normal range of distances and angles observed for cyclohexyl-substituted silsesquioxane frameworks.[2]

Trifluoride **3** is surprisingly resistant to hydrolysis. It is indefinitely stable in air, and it is uneffected by refluxing in $CDCl_3$ (65 °C, 4 h) with water/pyridine. However, net hydrolysis can be accomplished in two steps by reacting **3** with $Me_3SnOH$ ($CDCl_3$, 65 °C, 12 h) to produce **4**, which can be subsequently hydrolyzed to **5** with aqueous HCl.[24] Both reactions occur in nearly quantitative yield with complete retention of stereochemistry at the framework silicon atoms. Overall, the three-step isomerization of trisilanol **1** to pure trisilanol **5** can be easily accomplished in multigram quantities with yields in excess of 95%.

Benzene-$d_6$ solutions of **3** do not react with Grignard reagents (e.g., PhMgBr in THF) at temperatures as high as 110 °C, but the addition of MeLi to a solution of **3** in $Et_2O$ rapidly produces quantitative NMR yields of **6**.[24] As in the case of **3**, the stoichiometry of **6** was firmly established on the basis of multinuclear NMR data, but unambiguous assignment of the stereochemistry required a single crystal X-ray diffraction study.[26] We have not explored the generality of this reaction, but the high yield and stereospecificity observed with MeLi bodes well for the use of fluorine-substituted silsesquioxanes as precursors to mixed silsesquioxane/siloxane frameworks.

Substitution reactions at silicon have been extensively studied, and reasonable mechanisms have been suggested to rationalize

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(24) Detailed experimental procedures for the synthesis and characterization of all new compounds are provided in the Supporting Information.
(25) Crystal data for **3**: $[C_{42}H_{77}F_3O_9Si_7$ (fw 979.67)]: orthorhombic *Pbca*, $a$ = 21.308(6) Å, $b$ = 21.332(8) Å, $c$ = 22.790(7) Å; $V$ = 10359(6) Å$^3$; $D_{calc}$ = 1.256 g/cm$^3$ ($Z$ = 8). A total of 3714 independent reflections were collected on a Siemens P4 diffractometer at 163 K with use of graphite monochromated Mo Kα radiation. The final $R$ factor was 9.71% for the 1682 observed reflections with $F > 4\sigma(F)$. All other details of the crystal structure are reported in the Supporting Information.
(26) It was expected that **3** and **6** could crystallize in the same space group, but this is not the case. Crystal data for **6**: $[C_{43}H_{86}O_9Si_7$ (fw 967.77)]: cubic *Pa*3, $a = b = c$ = 22.1047(14) Å; $V$ = 10801(1) Å$^3$; $D_{calc}$ = 1.190 g/cm$^3$ ($Z$ = 8). A total of 2364 independent reflections were collected on a Siemens P4 diffractometer at 168 K with use of graphite monochromated Mo Kα radiation. The final $R$ factor was 25% for the 969 observed reflections with $F > 2\sigma(F)$. All other details of the crystal structure, including reasons for the high $R$ factor, are reported in the Supporting Information.

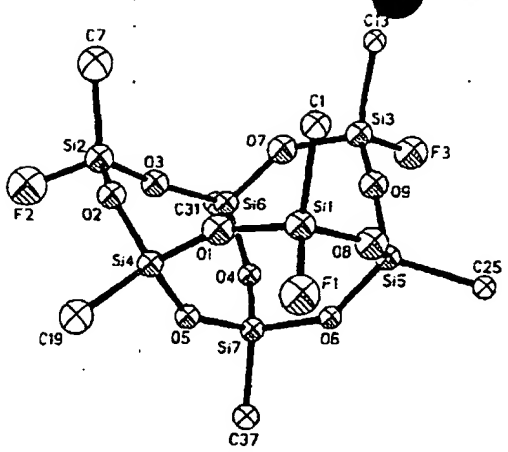


Figure 1. ORTEP plot of 3. For clarity, thermal ellipsoids are plotted at 50% probability, and only C's attached to Si's are shown.

the highly stereoselective outcomes of many reactions.[27-29] Numerous factors can influence the course of a reaction, and the overall stereochemical outcome of substitution is usually determined by the relative rates of competing pathways for inversion or retention of configuration.[28] In general, stereochemical inversion is favored with good leaving groups and/or weakly nucleophilic (i.e., "soft") reagents. However, cyclic silicon compounds often show a greater preference for retention of stereochemistry than open-chain analogs; for example, the acetolysis of cyclic chlorosiloxanes in acetic acid/acetic anhydride appears to proceed with a high degree (>92%) of stereochemical retention.[30] For the reaction of **1** with $HBF_4 \cdot OMe_2$, the formation of **3** with net inversion of stereochemistry at Si parallels the known reactions of silanols ($R_3SiOH$), silyl ethers ($R_3SiOR'$), and silyl amines ($R_3SiNHR$) with $BF_3$.[31] In each of these cases, the presence of strongly Lewis acidic boron centers facilitates loss of the leaving group via coordination while preventing the formation of strong nucleophiles. Both effects favor substitution with net inversion of stereochemistry at silicon; protons from strongly acidic $HBF_4$ should behave similarly.[27-29,32]

It is tempting to propose that an excess of $BF_3$ in commercial (Aldrich) $HBF_4$ etherate might be the actual fluorinating agent, but this suggestion is inconsistent with $^{19}F$ NMR data as well as the observation that the room temperature reaction of **1** with $BF_3$ (either alone or as an etherate) is slow and complicated by the formation of numerous decomposition products. On the basis of preliminary mechanistic studies, we suspect that $HBF_4$ is indeed the fluorinating agent and that a slight excess of $BF_3$ is required to prevent small amounts of HF from destroying the silsesquioxane framework. Whatever the mechanism, it is clear that the rapid, high yield formation of **3** requires *both* $HBF_4$ and $BF_3$.

The reactions of **3** with $Me_3SnOH$ and MeLi both proceed with complete retention of stereochemistry at silicon. Although the mechanistic details for nucleophilic substitution of these very different reagents are not clear, both results are consistent with the general observation that silyl fluorides react with hard nucleophiles (e.g., alkyl lithium reagents) to give substitution with net retention of stereochemistry at silicon.[27-29,33]

The synthetic transformations reported in this paper provide a potentially powerful new methodology for synthetically manipulating silsesquioxane frameworks. Although the generality of this methodology remains to be explored, both the stereospecific nature of these transformations and the facility with which they occur allow unprecedented synthetic manipulation of incompletely condensed silsesquioxane frameworks. Our efforts to expand the scope of these reactions will be reported in a future article.

**Acknowledgment.** These studies were supported by the National Science Foundation and Phillips Laboratory (Edwards AFB).

**Supporting Information Available:** A listing of experimental procedures and supporting characterization data for the synthesis of all new compounds and X-ray data for **3** and **6**, including experimental procedures, tables of crystal data, atomic coordinates, thermal parameters, bond lengths, angles, and ORTEP figures (24 pages). See any current masthead page for ordering and Internet access instructions.

JA963904M

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